Original Research

Conversion Pathways of DDT and Its Derivatives during Catalytic Hydrodechlorination

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Abstract

Di-1,1-chlorophenyl-2,2,2-trichloroethane (DDT) and its derivatives di-1,1-chlorophenyl-2,2-dichloroethane (DDD), di-1,1-chlorophenyl-2,2-dichloroethene (DDE), and di-1,1-chlorophenyl-2-chloroethene (DDMU) were dechlorinated in heptane solution over a sulphide Ni-Mo/C catalyst in a batch reactor. The process was carried out at 150-260ºC and hydrogen pressure of 3 MPa. For DDT, fast elimination of chlorine was observed from the aliphatic position, yielding mainly DDD at 150ºC. At around 200ºC, the aromatic chlorine atoms started to be removed. The complete dechlorination of the DDT derivatives was observed at 260ºC, yielding predominantly 1,1-diphenylethane (DPE) and 1,2-diphenylethane (BB). The conversion of DDT to BB was found to proceed via DDD. BB was presumably formed via carbenoid rearrangement of geminal dichlorides. Small amounts of diphenylmethane (DPM) were also found in the final product. Based on the GC-MS and GC-FID analyses of reaction products, the pathways of DDT derivative degradations during hydrodechlorination (HDCl) were proposed.

Keywords: insecticide, DDT, hydrodechlorination, Ni-Mo/C catalyst

Introduction

DDT has been used extensively worldwide as an insecticide for agriculture. Due to concern about its toxicity, the use of DDT is banned in most countries. However, in some developing countries, DDT is still used in quantities ranging from a few to several thousand tons. DDT is one of the 12 persistent organic pollutants selected by the Stockholm Convention of Persistent Organic Pollutants. Therefore, there is a need for the development of efficient method of DDT degradation.

Chlorine-containing organic compounds are commonly destroyed by high-temperature combustion. A basic problem with this method is the proven possibility of yielding harmful byproducts, including polychlorinated dibenzodioxins and dibenzofurans [1, 2]. The hydrodechlorination (HDCl) of chloroorganic compounds under reductive conditions using gaseous hydrogen and catalysts containing Ni, Ni-Mo and Co-Mo, can be considered an environmentally safe method [3]. In this case, the main reaction products of this process are hydrocarbons and HCl, which are easy to separate. In contrast to chlorobenzene [4] and polychlorinated biphenyls (PCBs) [5], knowledge about the catalytic hydrogenolysis of DDT and its derivatives during the HDCl process is scarce. A classical pathway of hydrogenolysis of DDT molecules assumes a progressive step-by-step removal of chlorine atoms. In general, under mild conditions chlorine is eliminated from the aliphatic position, whereas at higher temperatures it is removed from the aromatic position [6, 7]. The elimination of the first chlorine atom of DDT from the aliphatic position yields DDE, which can be hydrogenated to DDD *in situ*. It also reported the possibility of direct hydrodechlorination of DDT to DDD in the presence of metal catalyst [8]. Exhaustive hydrodechlorination of DDT leads to 1,1-diphenylethane.

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It is accepted that dechlorination of chloroalkanes on a nickel catalyst is preceded by an E1 elimination mechanism to form alkenes – dehydrochlorination [9]. Chlorine is bound by the surface of metallic catalyst-forming inorganic chloride. This reaction does not require hydrogen. Hydrogen is necessary for desorption of chlorine as HCl from the catalyst surface. Whereas dechlorination of chloroaromatic compounds proceeds by an electrophilic substitution reaction – hydrodechlorination [10-12]. Generally, the presence and position of both electron-donating and electron-withdrawing substituents affects the hydrodechlorination reaction rate according to the electrophilic mechanism theory [13, 14]. However, in some cases steric and electronic effects can also overlap. Hydrodechlorination of aromatic compounds effectively occurs in the temperature range 330-400ºC [15-17] in the presence of carbon/alumina-supported Ni catalyst. For comparison, complete dechlorination of chlorobenzene proceeds at temperatures higher than 490ºC, when only activated carbon was used without metallic phase.

Murena and Gioia [18] studied the kinetics of HDCl reaction for 2,4'-DDT and 4,4'-DDT using a commercial sulphide alumina-supported Ni-Mo catalyst at temperatures of 150-230ºC. They concluded that the destruction rate of DDT by catalytic hydrotreatment is significantly higher than that of chlorobenzene and PCBs. We have previously reported [19] that the complete dechlorination of 4,4'-DDT occurs in the presence of a sulphide Ni-Mo/C catalyst when the reaction is carried out at 200ºC with a hydrogen pressure of 3 MPa in a flow reactor. Activated carbon was chosen as a support due to its resistance to HCl. To have a deeper insight into conversion of DDT during HDCl process, both DDT and its derivatives such as DDD, DDE and DDMU were tested in this work using the same Ni-Mo/C catalyst in a stirred batch reactor.

Materials and Methods

4,4'-DDT (DDT), 4,4'-DDD (DDD), 4,4'-DDE (DDE), 4,4'-DDMU (DDMU) and hexadecane were purchased from the Aldrich company. Heptane, used as a solvent-reaction medium, was purchased from POCh Gliwice.

Catalyst Preparation

NiMo/C catalyst was prepared by incipient wetness method using commercial activated carbon (BAX 1500E Westvaco), ammonium molybdate tetrahydrate $[(NH_4)_6 \cdot Mo_7O_{24}] \cdot 4H_2O$ from Aldrich and nickel nitrate hexahydrate $[Ni(NO_3)_2] \cdot 6H_2O$ from POCh Gliwice. The composition of active phase was 5 wt% NiO and 15 wt% MoO_3. SEM-EDX examination revealed that Ni and Mo are homogeneously distributed on the surface of activated carbon. The tested catalyst was characterized by total pore volume of 0.989 cm^3 g^{-1} with comparable contribution of micro- and mesopores [19].

Hydrodechlorination Process

The HDCl reactions were conducted in microautoclave under hydrogen pressure of 3 MPa at 120-260ºC. 12 mL of substrate solution (1,500 mg/L) and 50 mg of catalyst were placed into a reactor in each experiment. Before the HDCl process, the catalyst had been sulphided with 75 μL of diethyl sulphide at 320ºC for 45 min. Afterwards the reactor was cooled to the temperature which was required for the process and the reaction substrate was injected into the reactor. The reaction mixture was kept homogenous with a magnetic stirrer. After the reaction the reactor was immediately cooled to room temperature. The HDCl degree was determined as an average of two runs.

Analysis of Reaction Products

The reaction products were analyzed using GC-MS, with a Hewlett Packard 6890 coupled to an MSD 5973 mass spectrometry detector. The samples were analyzed using the split injection method of 1 μl of sample with an HP-5 column (30 m x 0.25 mm x 0.25 μm film thickness). Helium was used as carrier gas. The initial temperature of the GC oven was 60ºC. This temperature was held for 1 min., then increased at a rate of 20ºC min^{-1} to 220ºC, and then held constant at this maximum temperature for 15 min. The injector temperature was 250ºC with a split of 5, and a constant pressure of 100 kPa.

Quantitative analysis was performed with a Hewlett Packard 5890 GC with an FID detector. The same parameters as GC-MS analysis were introduced for GC-FID, including oven temperature program, column, and pressure. FID detector provides signals proportional to a number of carbon atoms in the molecule analyzed. As such, the signals of different DDT derivatives were treated as providing the same intensity regardless of the number of chlorine atoms in the molecule. The temperature of FID detector was 250°C. Again, hexadecane was used as an internal standard. All samples were analyzed by GC-MS prior to quantitative analysis. Relative standard deviation of duplicate GC measurements of concentrations was < 5%.

The symbols and chemical structures of DDT and its derivatives are shown in Fig. 1.

Results and Discussion

Dechlorination of DDT

A scheme of dechlorination for DDT using Ni-Mo/C in a stirred batch reactor at temperatures between 120 and 260ºC, and a hydrogen pressure of 3 MPa is shown in Fig. 2. At 120ºC, a partial dechlorination of DDT to DDD was observed. Moreover, a trace amount of the compound with only aromatic chlorine atoms, i.e. di-1,1-chlorophenylethane (DCPE), was detected in the reaction products. The replacement of an aliphatic chlorine atom with a hydrogen atom was observed to proceed further at the higher temperature of 150ºC.
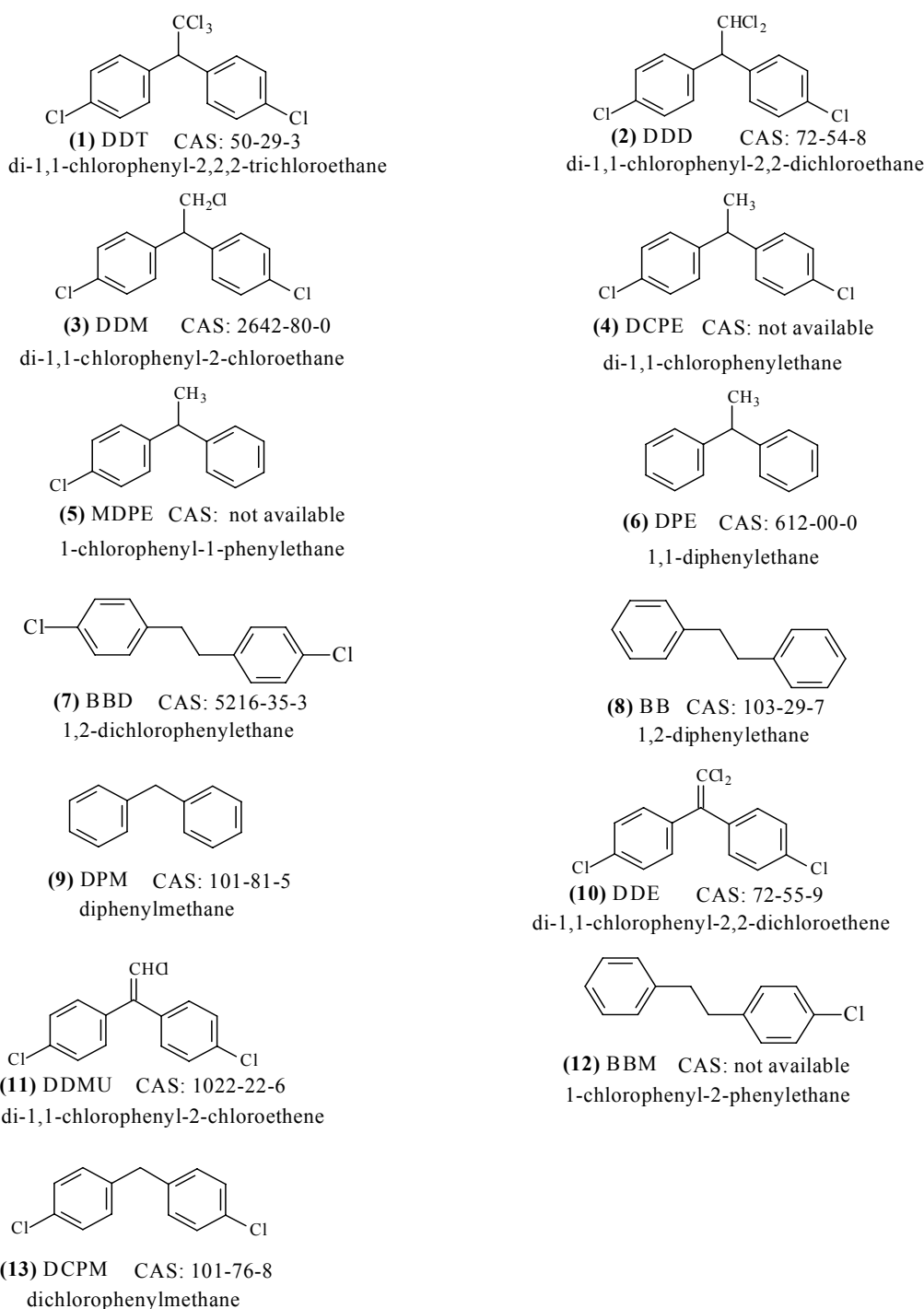
CCl₃ → CCl_3

(1) DDT   CAS: 50-29-3
di-1,1-chlorophenyl-2,2,2-trichloroethane

(2) DDD   CAS: 72-54-8
di-1,1-chlorophenyl-2,2-dichloroethane

(3) DDM   CAS: 2642-80-0
di-1,1-chlorophenyl-2-chloroethane

(4) DCPE   CAS: not available
di-1,1-chlorophenylethane

(5) MDPE   CAS: not available
1-chlorophenyl-1-phenylethane

(6) DPE   CAS: 612-00-0
1,1-diphenylethane

(7) BBD   CAS: 5216-35-3
1,2-dichlorophenylethane

(8) BB   CAS: 103-29-7
1,2-diphenylethane

(9) DPM   CAS: 101-81-5
diphenylmethane

(10) DDE   CAS: 72-55-9
di-1,1-chlorophenyl-2,2-dichloroethene

(11) DDMU   CAS: 1022-22-6
di-1,1-chlorophenyl-2-chloroethene

(12) BBM   CAS: not available
1-chlorophenyl-2-phenylethane

(13) DCPM   CAS: 101-76-8
dichlorophenylmethane

Fig. 1. Chemical structure of DDT and its derivatives. Retention time and molecular ion peak of compounds are:
(1) 17.13 min, m/z 354 (M+, 2.3%), 235(M-CCl₃, 100%);
(2) 15.27 min, m/z 320 (M+, 2.3%), 235 (M-CHCl₂, 100%);
(3) 13.4 1min, m/z 284 (M+, 7.0%), 235 (M-CH₂Cl);
(4) 10.98 min, m/z 250 (M+, 34%), 235 (M-CH₃, 100%);
(5) 9.49 min, m/z 216 (M+, 43%), 201 (M-CH₃, 100%);
(6) 8.28 min, m/z 182 (M+, 37%), 167 (M-CH₃, 100%);
(7) 11.28 min, m/z 250 (M+, 12%), 125 (M-C₇H₆Cl, 100%);
(8) 8.48 min, m/z 182 (M+, 26%), 91 (M-C₇H₇, 100%);
(9) 7.89 min, m/z 168 (M+, 100%), 91 (M-C₇H₇, 19%);
(10) 13.94min, m/z 318 (M+, 79%), 246 (M-Cl₂, 100%);
(11) 12.88 min, m/z 282 (M+, 66%), 212 (M-2Cl, 100%);
(12) 9.71 min, m/z 216 (M+, 33%), 91 (M-C₇H₆Cl, 100%);
(13) 10.53 min, m/z 236 (M+, 44%), 201 (M-Cl, 100%).

DDD and DCPE were the main products of dechlorination at this temperature. Only trace amounts of the initial compound DDT and di-1,1-chlorophenyl-2-chloroethane (DDM) were found. At 150°C, the chlorine atoms attached on the benzene ring remained intact. Dehydrohalogenation reactions, leading to unsaturated structures, were not observed. This type of reaction is not favored by high hydrogen pressure and the hydrogenating characteristics of the Ni-Mo catalytic system.

The reaction mixture at 200°C created a more complicated assembly. It consists of the compounds formed as a result of removing both aliphatic and aromatic chlorine atoms. DDD, DDM, and dichlorophenylmethane (DCPM) were found in trace amounts, and only DCPE was detected in significant quantities, being the product of complete replacement of aliphatic chlorine atoms with hydrogen atoms. The presence of 1-chlorophenyl-1-phenylethane (MDPE) and DPE proves that mono- and di-hydrodechlo-
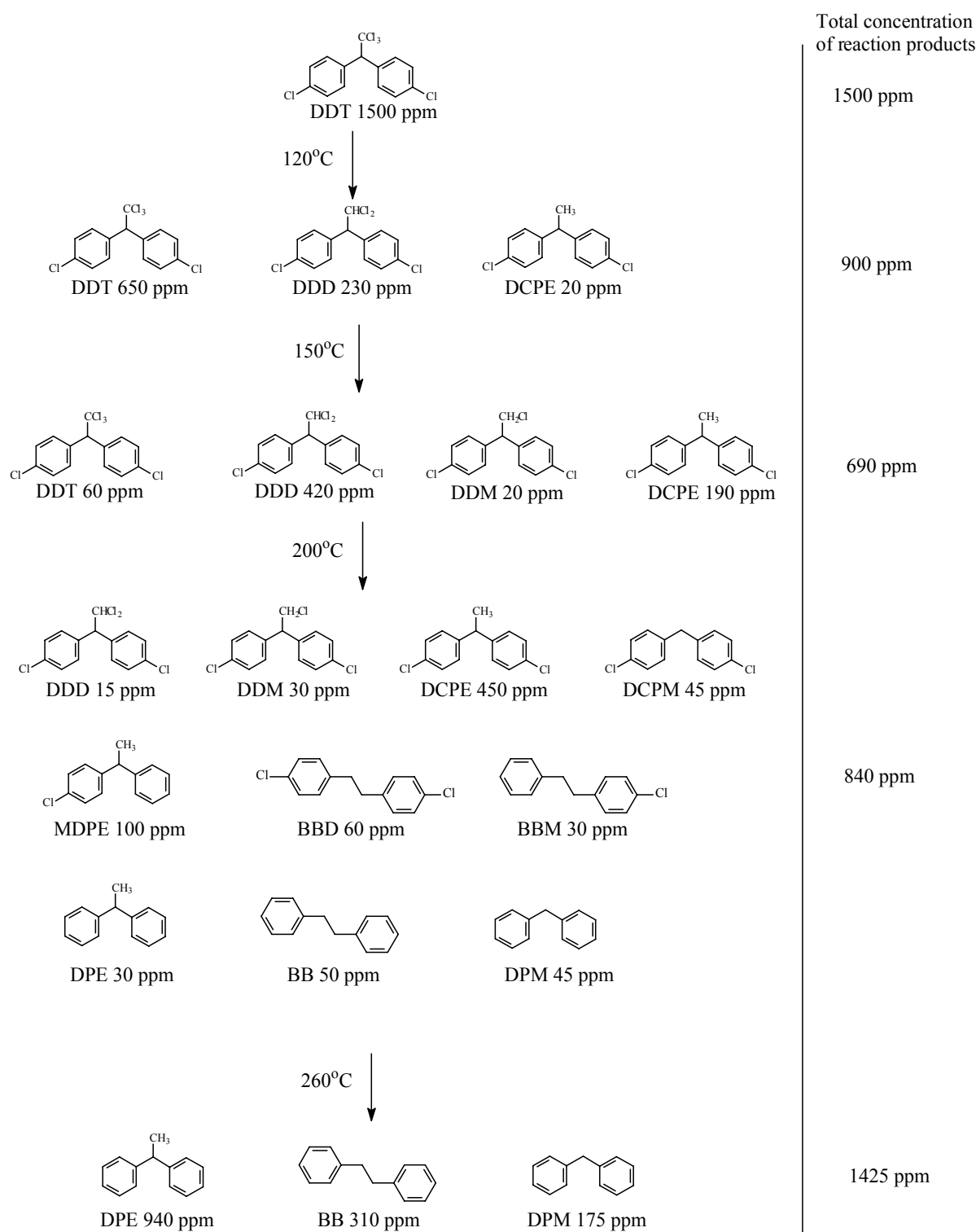

Fig. 2. Ni-Mo/C–catalyzed degradation of DDT *versus* temperature; hydrogen pressure 3 MPa, reaction time 1 h.

rination, respectively, from the benzene ring started to proceed. Moreover, the unexpected compounds such as 1,2-diphenylethane (BB) and its derivatives, 1,2-dichlorophenylethane (BBD) and 1-chlorophenyl-2-phenylethane (BBM), were detected. This suggests the rearrangement consisting in phenyl ring transfer from position 1 to 2 that have not been reported so far in the case of catalytic dechlorination of DDT under high hydrogen pressure. A similar rearrangement was observed by [20] in a process in which DDD was transformed to asymmetrical stilbene (trans-1,2-diphenylethene) in the presence of Vitaminum B_{12s} as a catalyst. Geminal dichlorides are needed as a metal-carbenoid precursor, postulated as intermediacy for carbenoid rearrangements. In our work the hydrogenating conditions of the process lead to saturated hydrocarbons and the formation of DDD from DDT *in situ*. A trace amount of DPM also was detected. DPM derivatives are supposed to be formed via thermocatalytic degradation of the aliphatic C-C bond, which is favored by inductive interaction of the chlorine atoms. The characteristic primary dissociation of the aliphatic C-C bond was observed in the mass spectrum of the degradation products of saturated DDT derivatives. DDT disappeared when the process was carried out at 200ºC under high hydrogen pressure using Ni-Mo/C catalyst.
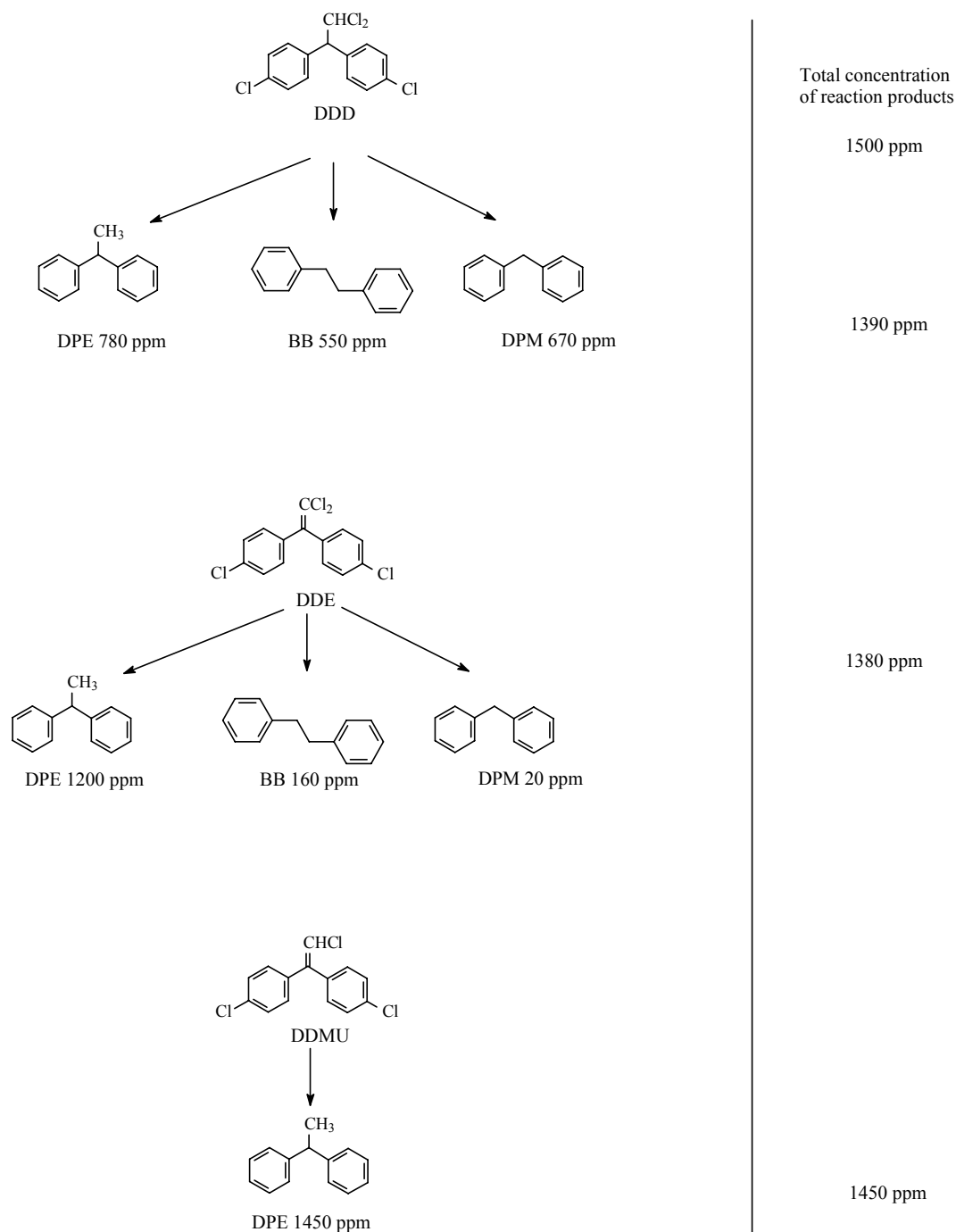

Fig. 3. Ni-Mo/C–catalyzed degradation of DDD, DDE and DDMU at 260ºC; hydrogen pressure 3 MPa, reaction time 1 h.

The complete dechlorination of DDT was achieved at 260°C, yielding three hydrocarbon species: diphenylethane (DPE) – 63%, bibenzyl (BB) – 21% and diphenylmethane (DPM) – 12%.

Hydrodechlorination reaction dominates under high hydrogen pressure in the presence of sulphided Ni-Mo/AC catalyst. Unsaturated intermediates that can form as a result of thermal elimination (dehydrodechlorination) [7] were not detected. Dehydrochlorination of DDT is the major pathway in the natural environment that leads to DDE.

The quantitative analysis of reaction products (Fig. 2) indicated that the depletion of reagents in the liquid phase occurs during the HDCl process in the presence of carbon-supported Ni-Mo catalyst. At 120ºC, the depletion of reagents was 40% and reached a maximum of 54% at 150ºC. At 260ºC, it was only 5%. When the HDCl process was carried out in the presence of carbon support only, this phenomenon was not observed. This suggests that the depletion of reagents/products is probably due to chemisorption on the active Ni-Mo phase. At a sufficiently high temperature (as high as 260ºC) the extent of depletion is small.

Dechlorination of DDD, DDE and DDMU

A scheme of dechlorination pathways for selected DDT derivatives over the Ni-Mo/C catalyst at 260°C and hydrogen pressure of 3 MPa is shown in Fig. 3. As shown above, DDD was formed in the first stage of the degradation of DDT as a main product of the dechlorination reaction. Thus, the products of exhaustive dechlorination of DDD were similar to those from DDT dechlorination. The reaction products at 260°C were DPE – 52%, BB – 37% and DPM – 4%. It can be noticed that the BB/DPE ratio was higher than that of the reaction with DDT as the starting material (0.71 vs 0.33). Compared to DDD dechlorination, the unsaturated derivative DDE yielded the same reaction products but with different concentrations. DPE is preferentially formed (80%) in the hydrodechlorination of DDE. A smaller amount of BB in the reaction products suggests that the molecular hydrocarbon skeleton rearrangement by phenyl ring transfer took place, but to a lesser extent than for DDD.

BB was probably formed via carbenoid rearrangement. This can be supported by the fact that BB was only formed when the substrata of the reaction was a compound with geminal chlorine atoms at the aliphatic carbon such as DDD, which is not the case of DDMU. It should be emphasized that DDT underwent fast dechlorination to DDD.

At 260ºC, DDMU was completely transformed to DPE. Neither molecular rearrangement by phenyl ring transfer, leading to BB, nor dissociation of the chloromethyl group =CClH leading to DPM were observed.

Conclusions

The complete dechlorination of DDT was achieved in the presence of a sulphide Ni-Mo/C catalyst in a stirred batch reactor under relatively mild conditions, i.e. at 260ºC

and hydrogen pressure of 3 MPa. At 120°C the removal of chlorine started with chlorine in aliphatic positions. Aromatic chlorine atoms were substituted by hydrogen at temperatures around 200°C. The final product consisted of DPE (63%), BB (21%), and DPM (12%).

The presence of DPM can be explained by cleavage of the C1-C2 bond that is favored by highly electronegative chlorine atoms at the C2 carbon. This process was inhibited in the presence of a double bond between carbons C1 and C2. Hence, the DPM content in the reaction products of dechlorination process decreased as follows: DDT > DDD > DDE, and was zero for DDMU.

The absence of unsaturated structures in the products of catalytic dechlorination of DDT and its derivatives proves that the process studied proceeded in strong hydrogenating conditions.

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